

8. REFINEMENT OF STRUCTURAL PARAMETERS

 8.7.3.4.2.2. *Electrostatic potential outside a charge distribution*

Hirshfelder, Curtiss & Bird (1954) and Buckingham (1959) have given an expression for the potential at a point \mathbf{r}_i outside a charge distribution:

$$\Phi(\mathbf{r}_i) = \frac{q}{r_i} + \frac{\mu_\alpha r_\alpha}{r_i^3} + \frac{1}{2} [3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}] \frac{\Theta_{\alpha\beta}}{r_i^5} + [5r_\alpha r_\beta r_\gamma - r^2 (r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\gamma\alpha} + r_\gamma \delta_{\alpha\beta})] \frac{\Omega_{\alpha\beta\gamma}}{5r_i^7} + \dots, \quad (8.7.3.61)$$

where summation over repeated indices is implied. The outer moments q , μ_α , $\Phi_{\alpha\beta}$ and $\Omega_{\alpha\beta\gamma}$ in (8.7.3.61) must include the nuclear contributions, but, for a point outside the distribution, the spherical neutral-atom densities and the nuclear contributions cancel, so that the potential outside the charge distribution can be calculated from the deformation density.

The summation in (8.7.3.61) is slowly converging if the charge distribution is represented by a single set of moments. When dealing with experimental charge densities, a multicentre expansion is available from the analysis, and (8.7.3.61) can be replaced by a summation over the distributed moments centred at the nuclear positions, in which case r_i measures the distance from a centre of the expansion to the field point. The result is equivalent to more general expressions given by Su & Coppens (1992), which, for very large values of r_i , reduce to the sum over atomic terms, each expressed as (8.7.3.61). The interaction between two charge distributions, A and B , is given by

$$E_{AB} = \int \Phi_A(\mathbf{r}) \rho_B(\mathbf{r}) d\mathbf{r},$$

where ρ_B includes the nuclear charge distribution.

 8.7.3.4.2.3. *Evaluation of the electrostatic functions in direct space*

The electrostatic properties of a well defined group of atoms can be derived directly from the multipole population coefficients. This method allows the ‘lifting’ of a molecule out of the crystal, and therefore the examination of the electrostatic quantities at the periphery of the molecule, the region of interest for intermolecular interactions. The difficulty related to the origin term, encountered in the reciprocal-space methods, is absent in the direct-space analysis.

In order to express the functions as a sum over atomic contributions, we rewrite (8.7.3.51), (8.7.3.54) and (8.7.3.57) for the electrostatic properties at point P as a sum over atomic contributions.

$$\Phi(\mathbf{R}_P) = \sum_{M \neq P} \frac{Z_M}{|\mathbf{R}_{MP}|} - \sum_M \int \frac{\rho_{e,M}(\mathbf{r}_M)}{|\mathbf{r}_P|} d\mathbf{r}_M, \quad (8.7.3.62)$$

$$\mathbf{E}(\mathbf{R}_P) = - \sum_{M \neq P} \frac{Z_M \mathbf{R}_{MP}}{|\mathbf{R}_{MP}|^3} + \sum_M \int \frac{\mathbf{r}_P \rho_{e,M}(\mathbf{r}_M)}{|\mathbf{r}_P|^3} d\mathbf{r}_M, \quad (8.7.3.63)$$

$$\nabla \mathbf{E}_{\alpha\beta}(\mathbf{R}_P) = - \sum_{M \neq P} \frac{Z_M (3R_\alpha R_\beta - \delta_{\alpha\beta} |\mathbf{R}_{MP}|^2)}{|\mathbf{R}_{MP}|^5} + \sum_M \int \frac{\rho_{e,M}(\mathbf{r}_M) (3r_\alpha r_\beta - \delta_{\alpha\beta} |\mathbf{r}_P|^2)}{|\mathbf{r}_P|^5} d\mathbf{r}_M, \quad (8.7.3.64)$$

in which the exclusion of $M = P$ only applies when the point P coincides with a nucleus, and therefore only occurs for the central contributions. Z_M and \mathbf{R}_M are the nuclear charge and the position vector of atom M , respectively,

while \mathbf{r}_P and \mathbf{r}_M are, respectively, the vectors from P and from the nucleus M to a point \mathbf{r} , such that $\mathbf{r}_P = \mathbf{r} - \mathbf{R}_P$, and $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M = \mathbf{r}_P + \mathbf{R}_P - \mathbf{R}_M = \mathbf{r}_P - \mathbf{R}_{MP}$. The subscript M in the second, electronic part of the expressions refers to density functions centred on atom M .

Expressions for the evaluation of (8.7.3.62)–(8.7.3.64) from the charge-density parameters of the multipole expansion have been given by Su & Coppens (1992). They employ the Fourier convolution theorem, used by Epstein & Swanton (1982) to evaluate the electric field gradient at the atomic nuclei. A direct-space method based on the Laplace expansion of $1/|\mathbf{R}_P - \mathbf{r}|$ was reported by Bentley (1981).

 8.7.3.4.3. *Electrostatic functions of crystals by modified Fourier summation*

Expression (8.7.3.49) is an example of derivation of electrostatic properties by direct Fourier summations of the structure factors. The electrostatic potential and its derivatives may be obtained in an analogous manner.

In order to obtain the electrostatic properties of the total charge distribution, it is convenient to define the ‘total’ structure factor $F_{\text{total}}(\mathbf{h})$ including the nuclear contribution,

$$F_{\text{total}}(\mathbf{h}) = F_N(\mathbf{h}) - F(\mathbf{h}),$$

where $F_N(\mathbf{h}) = \sum_j Z_j \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_j)$, the summation being over all atoms j with nuclear charge Z_j , located at \mathbf{R}_j . If $\Phi(\mathbf{h})$ is defined as the Fourier transform of the direct-space potential, we have

$$\Phi(\mathbf{r}) = \int \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h}$$

and

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi^2 \int h^2 \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h},$$

which equals $-4\pi \rho_{\text{total}}$ according to the Poisson equation (8.7.3.59). One obtains with

$$\rho_{\text{total}}(\mathbf{r}) = \int F_{\text{total}}(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h}, \quad \Phi(\mathbf{h}) = +F_{\text{total}}(\mathbf{h})/\pi h^2, \quad (8.7.3.65)$$

and, by inverse Fourier transformation of (8.7.3.65),

$$\Phi(\mathbf{r}) = \frac{1}{\pi V} \sum F_{\text{total}}(\mathbf{h})/h^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \quad (8.7.3.66)$$

(Bertaut, 1978; Stewart, 1979). Furthermore, the electric field due to the electrons is given by

$$\mathbf{E}(\mathbf{r}) = -\nabla \Phi(\mathbf{r}) = -\nabla \int \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h} = 2\pi i \int \mathbf{h} \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h}.$$

Thus, with (8.7.3.65),

$$\mathbf{E}(\mathbf{r}) = \frac{2i}{V} \sum [F_{\text{total}}(\mathbf{h})/h^2] \mathbf{h} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (8.7.3.67a)$$

which implies

$$\mathbf{E}(\mathbf{h}) = \frac{2i}{h^2} \mathbf{h} F_{\text{total}}(\mathbf{h}).$$

Similarly, the \mathbf{h} Fourier component of the electric field gradient tensor with trace $4\pi \rho(\mathbf{r})$ is

$$[\nabla : \mathbf{E}](\mathbf{h}) = +4\pi^2 \mathbf{h} : \mathbf{h} \Phi(\mathbf{h}) = +4\pi \mathbf{h} : \mathbf{h} F_{\text{total}}(\mathbf{h})/h^2, \quad (8.7.3.67b)$$

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where $\mathbf{i} : \mathbf{k}$ represents the tensor product of two vectors. This leads to the expression for the electric field gradient in direct space,

$$[\nabla : \mathbf{E}](\mathbf{r}) = \frac{4\pi}{V} \sum \mathbf{h} : \mathbf{h} F_{\text{total}}(\mathbf{h})/h^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \quad (8.7.3.68)$$

(The elements of $\mathbf{h} : \mathbf{h}$ are the products $h_i h_j$.)

The components of \mathbf{E} and the elements of the electric field gradient defined by (8.7.3.67a) and (8.7.3.68) are with respect to the reciprocal-lattice coordinate system. Proper transforms are required to get the values in other coordinate systems. Furthermore, to get the traceless $\nabla \mathbf{E}$ tensor, the quantity $-(4\pi/3)\rho_e(\mathbf{r}) = -(4\pi/3V) \sum F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$ must be subtracted from each of the diagonal elements ∇E_{ij} .

The Coulombic self-electronic energy of the crystal can be obtained from

$$\begin{aligned} E_{\text{Coulombic, electronic}} &= \frac{1}{2} \int \int \frac{\rho_e(\mathbf{r})\rho_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \\ &= \frac{1}{2} \int \Phi_e(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}. \end{aligned}$$

Since $\int \Phi(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} = \int \Phi(\mathbf{h})F(\mathbf{h}) d\mathbf{h}$ (Parseval's rule), the summation can be performed in reciprocal space,

$$E_{\text{Coulombic, electronic}} = \frac{1}{2\pi V} \sum F^2(\mathbf{h})/h^2, \quad (8.7.3.69a)$$

and, for the total Coulombic energy,

$$E_{\text{Coulombic, total}} = \frac{1}{2\pi V} \sum F_{\text{total}}^2(\mathbf{h})/h^2, \quad (8.7.3.69b)$$

where the integral has been replaced by a summation.

The summations are rapidly convergent, but suffer from having a singularity at $\mathbf{h} = 0$ (Dahl & Avery, 1984; Becker & Coppens, 1990). The contribution from this term to the potential cannot be ignored if different structures are compared. The term at $\mathbf{h} = 0$ gives a constant contribution to the potential, which, however, has no effect on the energy of a neutral system. For polar crystals, an additional term occurs in (8.7.3.69a, b), which is a function of the dipole moment D of the unit cell (Becker, 1990),

$$E_{\text{Coulombic, total}} = \frac{1}{2\pi V} \sum F_{\text{total}}^2(\mathbf{h})/h^2 + \frac{2\pi}{3V} D^2. \quad (8.7.3.69c)$$

To obtain the total energy of the static crystal, electron exchange and correlation as well as electron kinetic energy contributions must be added.

8.7.3.4.4. The total energy of a crystal as a function of the electron density

One can write the total energy of a system as

$$E = e_c[\rho] + T + E_{xc}, \quad (8.7.3.70)$$

where T is the kinetic energy, E_{xc} represents the exchange and electron correlation contributions, and $E_c[\rho]$, the Coulomb energy, discussed in the previous section, is given by

$$E_c = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{R_{ij}} - \sum_i Z_i \Phi(\mathbf{R}_i) + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (8.7.3.71)$$

where Z_i is the nuclear charge for an atom at position \mathbf{R}_i , and $\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i$.

Because of the theorem of Hohenberg & Kohn (1964), E is a unique functional of the electron density ρ , so that $T + E_{xc}$ must be a functional of ρ . Approximate density functionals are discussed extensively in the literature (Dahl & Avery, 1984) and are at the centre of active research in the study of electronic structure of various materials. Given an approximate functional, one can estimate non-Coulombic contributions to the energy from the charge density $\rho(\mathbf{r})$.

In the simplest example, the functionals are those applicable to an electronic gas with slow spatial variations (the 'nearly free electron gas'). In this approximation, the kinetic energy T is given by

$$T = c_k \int \rho t[\rho] d^3\mathbf{r}, \quad (8.7.3.72)$$

with $c_k = (3/10)(2\pi^2)^{2/3}$; and the function $t[\rho] = \rho^{2/3}$. The exchange-correlation energy is also a functional of ρ ,

$$E_{xc} = -c_x \int \rho e_{xc}[\rho] d^3\mathbf{r},$$

with $c_x = (3/4)(3/\pi)^{1/3}$ and $e_{xc}[\rho] = \rho^{1/3}$.

Any attempt to minimize the energy with respect to ρ in this framework leads to very poor results. However, cohesive energies can be described quite well, assuming that the change in electron density due to cohesive forces is slowly varying in space.

An example is the system AB , with closed-shell subsystems A and B . Let ρ_A and ρ_B be the densities for individual A and B subsystems. The interaction energy is written as

$$\begin{aligned} \Delta E &= E_c[\rho] - E_c[\rho_A] - E_c[\rho_B] \\ &+ c_k \int d\mathbf{r} \{ \rho t[\rho] - \rho_A t[\rho_A] - \rho_B t[\rho_B] \} \\ &- c_x \int d\mathbf{r} \{ \rho e_{xc}[\rho] - \rho_A e_{xc}[\rho_A] - \rho_B e_{xc}[\rho_B] \}. \end{aligned} \quad (8.7.3.73)$$

This model is known as the Gordon–Kim (1972) model and leads to a qualitatively valid description of potential energy surfaces between closed-shell subsystems. Unlike pure Coulombic models, this density functional model can lead to an equilibrium geometry. It has the advantage of depending only on the charge density ρ .

8.7.3.5. Quantitative comparison with theory

Frequently, the purpose of a charge density analysis is comparison with theory at various levels of sophistication. Though the charge density is a detailed function, the features of which can be compared at several points of interest in space, it is by no means the only level at which comparison can be made. The following sequence represents a progression of functions that are increasingly related to the experimental measurement.

$$\begin{array}{ccccccc} & & \text{electrostatic} & & & & \\ & & \text{properties} & & & & \\ & & \uparrow & & & & \\ \psi(1, 2, \dots, n) & \rightarrow & \Gamma^1(1, 1) & \rightarrow & \rho(\mathbf{r}) & \rightarrow & \langle \rho(\mathbf{r}) \rangle \rightarrow F(\mathbf{h}) \rightarrow I(\mathbf{h}) \\ & & \downarrow & & & & \\ & & \Delta\rho(\mathbf{r}) & \rightarrow & \langle \Delta\rho(\mathbf{r}) \rangle, & & \\ & & & & & & (8.7.3.74) \end{array}$$

where the angle brackets refer to the thermally averaged functions.

The experimental information may be reduced in the opposite sequence: